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A perturbation theory of classical simple fluids

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Abstract The Weeks - Chandler - Andersen (W C A) perturbation theory of classical simple fluid is reexamined using the 'modified' Born - Green - Yvan expression for the function Y(r) of the hard sphere fluid We calculate the thermodynamic properties of the Lennard - Jones (12-6) fluid They are found to be in good agreement with the Verlet - Weis, Boublik and Simulation results

Keywords Perturbation theory, free energy, equation of state

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1. Introduction

Weeks – Chandler – Andersen (WCA) [1] perturbation theory with the semi empirical expression for the hard – sphere radial distribution function (RDF) $g_{HS}(r)$ [2,3] is in error in some applications. This difficulty can be avoided by using a better expression for $g_{HS}(r)$.

In the present work, we are primarily concerned with the WCA theory and the 'modified' Born – Green – Yvan (BGYM) expression for $Y_{HS}(r)$ for $r \le d$, obtained by Chae, Ree and Ree [4]. These values for $Y_{HS}(r)$ are in much better agreement than those of PY – values [5].

2. Theoretical formulation

We consider a system, whose molecules interact via the LJ (12-6) potential

$$u(r) = 4 \in \left[(\sigma / r)^{12} - (\sigma / r)^{6}\right], \tag{1}$$

where $\in$ and σ are constants with units of energy and length, respectively.

Using the division of potential according to the WCA scheme [1], the excess free energy per particle is given by

$$f = f_0 + f_1 , \tag{2}$$

where f_0 is the excess free energy per particle of the reference system and f_1 is the first order perturbation correction to it. Thus

$$f_1 = 2\pi\rho \int_0^\infty g_0(r)\, u_p(r)\, r^2 dr , \tag{3}$$

where $g_0(r)$ is the RDF of the reference system.

3. Reference system

The free energy of the reference system is expressed in terms of that of the hard spheres of diameter d, which can be determined by the Verlet-Weis method [2, 3].

In the present work, to evaluate d, we use the BGYM expression for $Y_{HS}(r/d)$, given as [4]

$$Y_{HS}(r/d) = g_{HS}(d) \exp\left[\pi \rho d^3 g_{HS}(d) \{ (1/12)(r/d)^2 - (r/d) + (11/12)\}\right] \text{for } r \le d , \tag{4}$$

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where $g_{HS}(d)$ is the hard sphere RDF at the contact and given by [6]

$$g_{HS}(d) = (1-\eta/2)/(1-\eta)^3, \tag{5}$$

where $\eta = \pi \rho d^3/6$ is the packing fraction. Then d is given by

$$d = d_B\left[1+(\sigma_1/2\sigma_0)\delta\right], \tag{6}$$

where

$$d_B = \int_0^\infty (1-\exp[-\beta u_0(r)])dr, \tag{7}$$

$$\delta = \int^\infty ((r/d_B)-1)^2 (d/dr)(\exp[-\beta u_0(r)])dr \tag{8}$$

and

$$\sigma_1/2\sigma_0 = (1-(11/2)\eta+(17/4)\eta^2+\eta^3)/(1-\eta)^3. \tag{9}$$

Only $\sigma_1/2\sigma_0$ differs from that derived by Verlet and Weis (VW).

The virial equation of state for the reference system is given by [2, 3]

$$\beta P_0/\rho \equiv Z_0 = Z_{HS} + 4\delta\,\Delta Z, \tag{10}$$

where Z_{HS} is the hard sphere compressibility factor and given by [6]

$$Z_{HS} = (1+\eta+\eta^2+\eta^3)/(1-\eta)^3 \tag{11}$$

and ΔZ is derived using the BGYM expression for $Y_{HS}(r/d)$

$$\Delta Z = -2\eta^2(1-\eta/2)^2/(1-\eta)^6 \tag{12}$$

which differs from that given by Verlet and Weis [2, 3].

With the help of eq. (10), we obtain an expression for the free energy per particle for the reference system

$$\beta f_0 = \beta f_{HS}^{ex} + 4\delta\beta\Delta f, \tag{13}$$

where [6]

$$\beta f_{HS}^{ex} = \eta(4-3\eta)/(1-\eta)^2 \tag{14}$$

is the excess free energy of the hard sphere system and

$$\beta\Delta f = (1/30)(\eta^2/(1-\eta)^3) - (1/8)(\eta^2/(1-\eta)^4)$$
$$-(1/10)(\eta/(1-\eta)^5) + (15/16)(\eta^2/(1-\eta)^6) \tag{15}$$

4. First order perturbation term

In the WCA theory, the RDF $g_0(r)$ of the reference system is approximated as [1]

$$g_0(r) \approx \exp[-\beta u_0(r)]\,Y_{HS}(r/d) \tag{16}$$

Substituting eq. (16) in eq. (3), we obtain

$$f_1 = 2\pi\rho \int^\infty Y_{HS}(r/d)\,u_p(r)\,r^2 dr + O(\delta). \tag{17}$$

In the present calculation, we use the MC [2, 3] and MD [2,3] values of $g_{HS}(r)$ for $r > d$.

5. Results and discussion

We compare our results of $\beta P/\rho$ and $\beta U/N$ for the LJ (12-6) fluid with VW [2], Boublik [7] and MC [2] values in a range of reduced density ρ^* at T* = 1.15 in Table 1. The agreement is quite good. At low density, Boublik theory [7] is superior to the present theory due to the second order perturbation terms.

Table 1. Values of $\beta P/\rho$ and $\beta U/N$ for the LJ (12-6) fluid at T* = 1.15

	ρ^*	Exact	Present	VW	Boublik
$\beta P/\rho$	0.30	0.12	0.05	0.05	0.05
	0.50	−0.13	−0.28	−0.27	−0.19
	0.65	0.31	0.17	0.17	0.23
	0.75	1.17	1.12	1.10	1.09
$\beta U/N$	0.30	−1.95	−1.60	−1.60	−1.83
	0.50	−3.02	−2.86	−2.86	−3.02
	0.65	−3.87	−3.89	−3.83	3.90
	0.75	−4.46	−4.42	4.43	−4.45

Thus we come to the conclusion that the WCA perturbation theory, using the BGYM integral equation for $Y_{HS}(r/d)$ for $r \leq d$, can be employed to calculate the equilibrium properties of simple fluid.

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